USING A POLYESTER BINDER FOR THE INTERLAMINAR TOUGHENING OF GLASS/EPOXY COMPOSITE LAMINATES

Lode Daelemans[1], Sam van der Heijden[1], Ives De Baere[2], Hubert Rahier[3], Wim Van Paepegem[2], Karen De Clerck[1*]

[1] Department of Textiles, Ghent University,
Technologiepark-Zwijnaarde 907, B-9052 Zwijnaarde, Belgium
Karen.DeClerck@UGent.be

[2] Department of Materials Science and Engineering, Ghent University,
Technologiepark-Zwijnaarde 903, B-9052 Zwijnaarde, Belgium

[3] Department Materials and Chemistry, Vrije Universiteit Brussel,
Pleinlaan 2, B-1050 Brussels, Belgium

Keywords: Binder/tackifier, Double cantilever beam, Fracture toughness, Vacuum assisted resin transfer moulding

ABSTRACT

Bisphenol A based polyester is commonly used in the industry as a binder, or tackifier, to produce cost-saving preforms in Liquid Composite Moulding processes such as Vacuum Assisted Resin Transfer Moulding (VARTM). However, it is often reported that the presence of these polyesters has a detrimental effect on the mechanical properties of the resulting composite laminates. This study shows that interlaminar toughness can be increased without negatively affecting other properties by a applying a bisphenol A based polyester binder. Both polyester modified epoxy resin as well as polyester modified glass/epoxy laminates are studied. It is shown that the presence of the polyester has a profound effect on the curing characteristics and glass transition temperature of the epoxy resin. Furthermore, fracture toughness experiments (Single Edge Notch Bending) show that there is an optimum polyester concentration which leads to a toughened epoxy matrix. Composite laminates are produced from binder coated glass fibre plies with VARTM. Double Cantilever Beam fracture experiments show that the polyester binder increases the Mode I interlaminar toughness by 60 %. Three point bending experiments show that the flexural properties were not negatively affected by the presence of the polyester in the interlaminar region between plies.

1. INTRODUCTION

Liquid Composite Moulding (LCM) processes such as Vacuum Assisted Resin Transfer Moulding (VARTM) have gained serious attention over the last decade since they offer the possibility for significant cost reductions for the production of composite materials compared to the traditional prepreg technology [1–5]. The LCM process consists of stacking dry textile reinforcements into a mould and injecting resin through this structure, followed by curing and demoulding of the composite. In order to reduce production time and costs, pre-shaped reinforcing structures, or preforms, can be used. They aid the stacking, alignment and placement of the textile reinforments in the mould cavity. These preforms consist out of several layers of stacked and aligned textile reinforcements with the appropriate shape which are usually bound together by using polymeric materials referred to as binders or tackifiers. The binder is deposited between the reinforcing plies and softens by applying heat. Pressure is applied during the thermoforming in order to achieve a certain thickness and fibre volume fraction of the preform. The binder will solidify upon cooling and adhere adjacent reinforcing plies together. Low melting thermoplastic polyesters are the most common available binders and sold commercially under names as ATLAC 363 (Reichold) or FILCO F661 (COIM group). The major drawback of using binder consolidated preforms is that they can have a detrimental effect on the

mechanical properties of the final laminates [6–10]. Previous research stated that especially the (Mode I) interlaminar fracture toughness is decreased upon addition of polyester binders in the composite laminates [6,9].

In the present study, we will show that by a proper selection of the amount of binder applied, the detrimental effects can be avoided and the mechanical properties can even be increased. This will be illustrated for unidirectional glass fibre plies coated with a common commercial binder system based on bisphenol A based thermoplastic polyester. The coated plies are used to produce interlayer toughened composite laminates by VARTM which are tested by Double Cantilever Beam (DCB) fracture experiments. Furthermore, the interaction between the polyester and the epoxy matrix resin is investigated by means of Differential Scanning Calorimetry (DSC) and Single Edge Notched Bending (SENB) fracture experiments.

2. MATERIALS AND METHODS

2.1 Materials

The investigated polyester binder is poly(4,4'-dipropoxy-2,2'-diphenyl propane fumarate), a powdered bisphenol A based polyester purchased from Scientific Polymer. The structure of the polyester is similar to that of commercial binder systems such as ATLAC 363E (Reichhold) and FILCO F661 (COIM group). The commercial binder system FILCO F661 was kindly provided by the COIM group. To exclude any unwanted effects due to fillers or additives in the commercial binder systems, poly(4,4'-dipropoxy-2,2'-diphenyl propane fumarate) is used as the main polyester binder in this study. The glass transition temperature (Tg) of the polyester is determined using DSC and is 52 °C, see Figure 1.

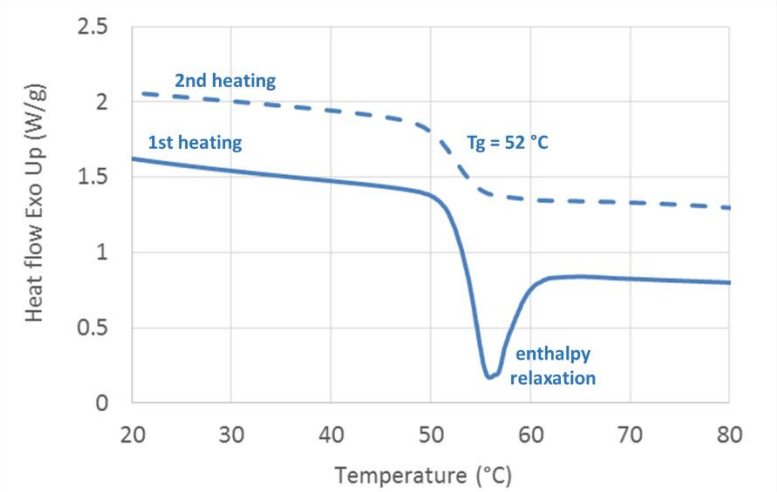

Figure 1: DSC thermogram of poly(4,4'-dipropoxy-2,2'-diphenyl propane fumarate).

Unidirectional E-glass plies with an areal density of 500 g/m², UDO ES500 manufactured by SGL Group, are used to produce composite laminates. The matrix is a low viscosity ductile epoxy/amine thermoset resin system EPIKOTE MGS RIM 135 purchased from Momentive commonly used for wind energy applications. This resin system consists out of a DGEBA epoxy and a diamine curing agent, EPIKURE MGS RIM H137. Epoxy resin and curing agent are mixed in a 10:3 volume ratio and cured for 24 hours at room temperature (23.2 °C, 50% RH) followed by a post-cure of 15 hours at 80 °C according to the manufacturer's instructions.

2.2 Effect of the polyester binder on GFRP composite laminates

The polyester powder is evenly distributed on the glass fibre plies and fixated to the glass fibres by heating the plies to 80 °C for 30 minutes without consolidation pressure. The binder coated glass fibre plies are used to produce composite laminates of 300 x 300 x 3 mm with an in-house VARTM setup consisting out of a two-piece flat mould. After infusion, the moulds are cured according to the manufacturer's recommended cure cycle. A $[0°]_8$ composite laminate is used to determine the Mode I interlaminar fracture toughness (G_{Ic}) with the Double Cantilever Beam method according to ASTM D5528. Prior to infusion, a release film is placed in the midplane of the laminate to serve as an initial delamination for the specimens. The glass fibre plies facing the midplane are coated only on the midplane-facing sides. DCB specimens are cut from the laminates with a water-cooled diamond saw to 150 x 20 x 3 mm. An Instron 5800R machine equipped with a load cell of 500 N is used in order to measure load and deflection; the crack front propagation is monitored using a travelling microscope. At least four specimens are tested for each configuration. A cross-ply $[90°/0°]_{2S}$ composite laminate is made with and without binder coated glass fibres for flexure testing in order to investigate the effect of the polyester on the (flexural) mechanical properties of the laminates. The glass fibre plies are coated with 3 wt% (wt% to glass fibre ply) on both sides of the plies. In each interlayer between two reinforcing plies, two binder coated glass fibre sides are facing each other. This ensured that the laminate layup is completely symmetric and any unwanted effects due to asymmetry are cancelled. The flexural properties of the laminates are obtained from 3-point bending tests according to ASTM D7264 on an Instron 5800R with a 10 kN load cell. The specimens are cut to 60 x 13 x 3 mm with a water-cooled diamond saw. The span to thickness ratio was 16:1.

2.3 Effect of the polyester binder on the curing behaviour and toughness of the matrix resin

The curing behaviour of the epoxy resin system is investigated by DSC and performed on a TA Instruments Q2000 Tzero™ DSC instrument. Epoxy resin and curing agent are mixed in a 10:3 volume ratio stirred mechanically for 3 minutes. Powdered polyester is added and the mixture is again mechanically stirred for 3 minutes. An amount of 10 - 15 mg of this mixture is then added in a DSC crucible which is hermetically sealed afterwards. The preparation of the DSC specimens is done at 23.2 °C and 50% RH. In order to minimise the curing before the start of the test, the experiments are carried out immediately after sealing the crucibles. A non-isothermal temperature ramp (20 °C to 250 °C at 5 °C/min) is selected to fully cure the epoxy resin and measure the reaction heat. A second temperature ramp from 20 °C to 150 °C is performed in order to measure the Tg of the cured epoxy. At least three specimens are tested for each configuration.

Specimens for SENB testing are prepared by casting resin mixed with powdered polyester in a steel mould. Before the polyester is added, the resin is put under vacuum to remove any trapped air due to mixing. Powdered polyester is added and mechanically stirred into the degassed resin. Any trapped air is removed and the mixture is casted in a steel mould of 80 x 80 x 20 mm. The manufacturer's recommended cure cycle is used to cure the resin. The specimens are carefully cut to 80 x 15 x 7.5 mm with a water-cooled diamond saw. The fracture toughness of the polyester modified epoxy resin is determined by flexure experiments on an electromechanical Instron 5800R machine with a load cell of 500 N according to ASTM D5045. A notch is milled in each specimen and a precrack is generated using a dynamic precracking method [11]. An Olympus BX51 optical microscope with an Olympus UC30 camera is used to inspect the crack surfaces of tested SENB specimens. In order to establish a baseline value for the fracture toughness of the virgin resin, ten SENB specimens are tested. At least three specimens are tested for other configurations.

3. RESULTS AND DISCUSSION

3.1 Effect of the polyester binder on GFRP composite laminates

3.1.1 Mode I interlaminar fracture toughness

The effect of the polyester on the interlaminar fracture toughness is determined by Double Cantilever Beam experiments on specimens produced as described in Section 2.2. The glass fibre plies are coated with the polyester in a range between 0.5 wt% and 6 wt% (wt% to glass fibre ply). This is in accordance with the range of polyester loadings commonly used in industry [10]. Several specimens are made with the commercial FILCO 661 binder system in order to compare it with the reference polyester binder. The results from the DCB experiments are visualised in Figure 7. Coating the reinforcing glass fibre plies with the polyester increases the Mode I interlaminar fracture toughness, both in initiation ($G_{Ic,ini}$) and propagation ($G_{Ic,prop}$). As expected, the effect of the commercial FILCO binder system is very similar to the polyester binder since both binders are also chemically similar. The interlaminar fracture toughness increases up to a polyester loading of around 3 wt% (3 wt% on each reinforcing ply facing the midplane). At even higher polyester loadings up to 6 wt%, the interlaminar fracture toughness stays more or less the same. The $G_{Ic,ini}$ increases from 410 J/m² to around 650 J/m² which is an increase of 58 %, while the $G_{Ic,prop}$ increases from 610 J/m² to 1000 J/m² which is an increase of almost 65 %.

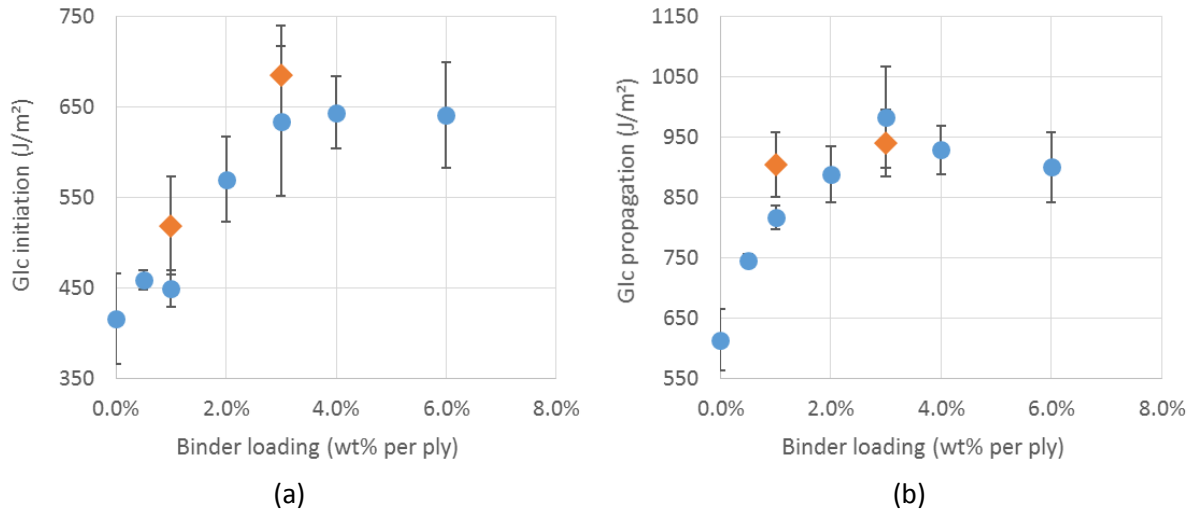

Figure 2: Mode I interlaminar fracture toughness in initiation (a) and propagation (b) for the polyester modified GFRP laminates (●) and FILCO F661 modified GFRP laminates (♦) show a steep increase in G_{Ic} up to 3 wt% (wt% to ply) of polyester after which G_{Ic} levels off.

3.1.2 Flexural properties

Flexural properties of an interlayer toughened laminate are determined according to ASTM D7264 with a three-point bending setup. Each side of the glass fibre plies is coated with 3 wt% (wt% to ply) polyester, which yielded the highest increase in Mode I interlaminar fracture toughness. There is no significant effect in flexural modulus or flexural strength between a virgin laminate and an interlayer toughened polyester modified laminate, see Table 1. Hence, the application of the bisphenol A based polyester leads to a large increase in interlaminar fracture toughness without negatively affecting the flexural stiffness and strength of the composite laminates.

	Flexural stiffness (GPa)	Flexural strength (MPa)
Virgin laminate	16.9 ± 0.4	594 ± 11
Polyester modified laminate	16.7 ± 0.9	601 ± 16

Table 1: Flexural properties of virgin and polyester modified GFRP laminates.

3.2. Effect of the polyester binder on the matrix resin

In order to explain the observed increase in Mode I interlaminar fracture toughness for GFRP laminates modified with polyester binder, the effect of the polyester binder on the matrix resin is determined. Since the polyester binder is mainly present in the interlaminar region between reinforcing plies, it can affect the resin locally in these regions. Therefore, the polyester binder – epoxy resin interaction is studied by DSC and SENB in the absence of glass fibre plies.

3.2.1 Curing behaviour and glass transition temperature

DSC experiments are carried out as explained in Section 2.3 on epoxy resin mixed with the polyester binder. The polyester binder loading is now expressed as wt% to resin as compared to previous sections where it was expressed as wt% to reinforcing ply. The loading range is, however, similar and comparable to the amounts of polyester used in an industrial setting [10]. Figure 3 (a) shows the glass transition temperature (Tg) as a function of polyester loading. The Tg decreases with increasing amount of polyester and levels off at higher polyester loadings (above 10 wt%). Figure 3 (b) shows the normalised curing heat, which is a measure for the conversion of the epoxy resin, in function of polyester loading. The polyester binder is amorphous and thus no heat related to melting of the binder is measured during the curing experiments. The curing heat decreases significantly at high polyester loadings (above 10 wt%) resulting in a partially cured resin. This could be due to a blocking of crosslinking-sites by polyester molecules or due to a hindered diffusion of epoxy and (amine) curing agent. Two zones can be identified from the results in Figure 3: initially the Tg decreases linear with polyester loading and the curing is hardly affected, while at high polyester loadings the Tg levels off and only partial curing of the resin is achieved. Furthermore, a second Tg around 52 °C was observed on the DSC thermograms at high polyester loadings, see Figure 4. Hence, at low polyester loadings there is a small plasticizing effect of the polyester on the epoxy resin. However, at high polyester loadings there is partial curing of the epoxy resin and a phase separation of the polyester into a polyester-rich second phase. In conclusion, at low polyester loadings the resulting mixture is a one-phase structure due to complete miscibility between the epoxy resin and the polyester molecules, while at higher loadings a second phase is formed which consists mainly out of polyester. This phase separation is very important as it could have a negative effect on the mechanical properties of the epoxy resin, due to the inherent brittleness of the polyester and the partial curing of the epoxy.

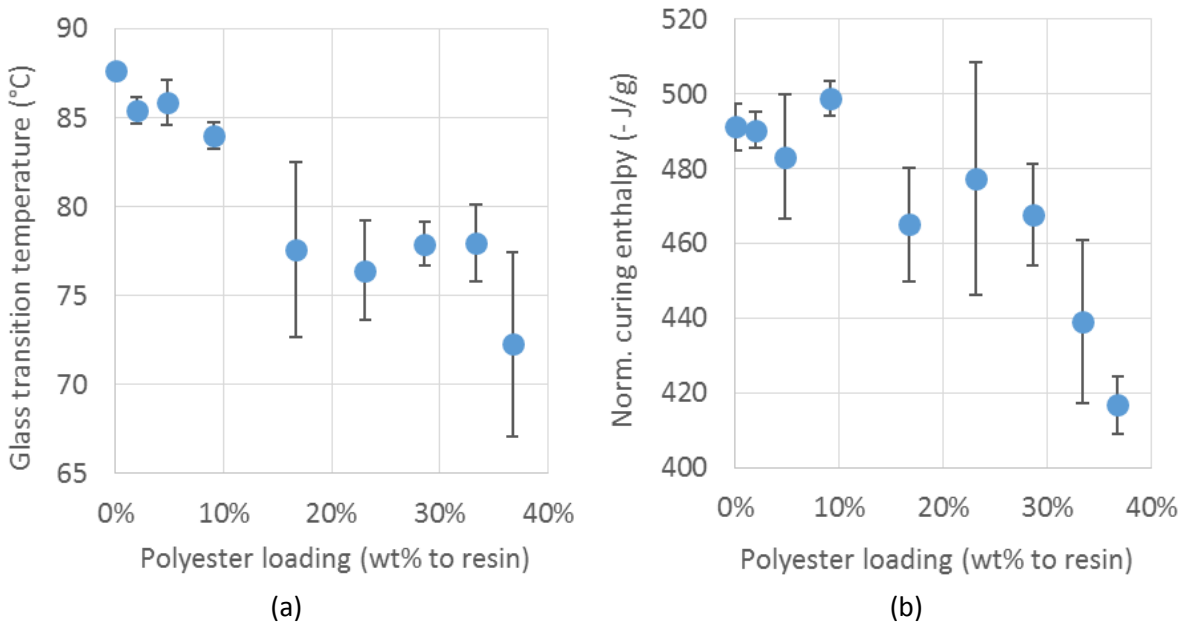

Figure 3: The Tg of the matrix resin decreases with increasing polyester loading (a). The curing enthalpy also decreases at high polyester loadings resulting in a partially cured resin (b).

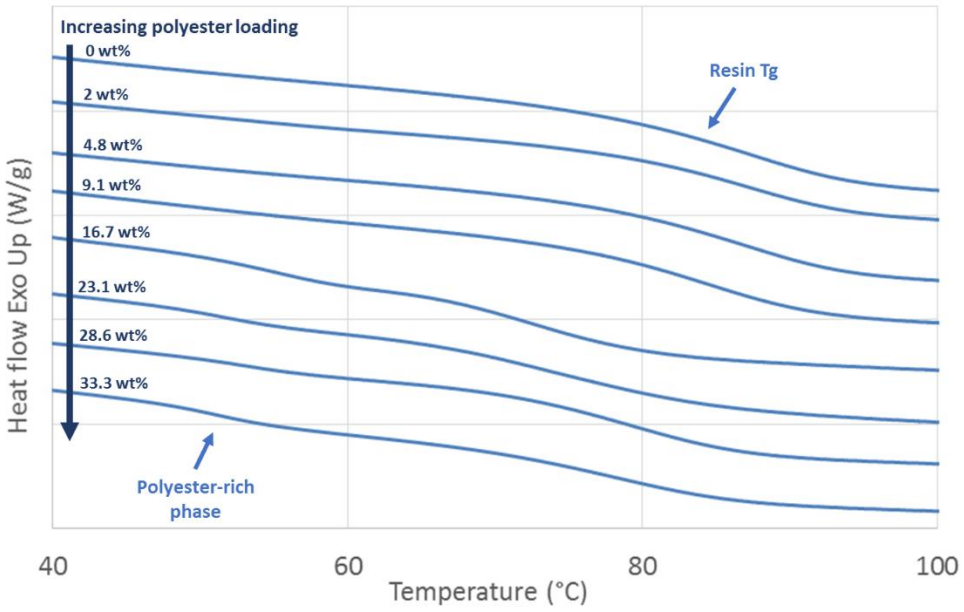

Figure 4: At high polyester loadings a second Tg-transition is observed around 52 °C indicating phase separation of the polyester binder into a polyester-rich phase.

3.2.2 Fracture toughness

The fracture toughness of the epoxy resin is determined by Single Edge Notched Bending fracture experiments as explained in Section 2.3. Section 3.2.1 shows that small amounts of polyester binder plasticize the matrix resin, while a polyester-rich phase is formed at high polyester loadings. These effects can affect the fracture toughness of the matrix resin. The RIMR 135 virgin epoxy resin is a very tough resin with a critical intensity factor K_{Ic} of 1.98 ± 0.12 MPa$\sqrt{m}$ and a fracture toughness G_{Ic} of 1590 J/m². The fracture toughness of the virgin resin is much higher than that of standard epoxy

resins or polyester resins which typically have a fracture toughness between 100 - 700 J/m² and is expected to be much higher than the bulk polyester binder's fracture toughness. The results of the SENB experiments are visualised in Figure 5 (a). For specimens containing 4.8 wt% of polyester binder the fracture toughness increases significantly compared to the virgin resin. A fracture toughness of about 2000 J/m² is obtained for these specimens. The increase in fracture toughness is mainly due to a small increase in failure strain of the epoxy resulting in a larger area underneath the load-displacement curve, see Figure 5 (b). The (macroscopic) failure of the polyester modified epoxy system remains brittle, even for the toughened 4.8 wt% specimens, as seen by the sudden drop in load on the load-displacement curves. The increase in failure strain can be explained by the plasticizing effect of the polyester on the epoxy matrix which makes the crosslinked epoxy network a little more flexible. At around 4.8 wt% of polyester, the added flexibility leads to an increased fracture toughness of the bulk resin. However, at higher polyester loadings, the immiscibility of the polyester in the epoxy resin results in the formation of a brittle polyester-rich second phase as discussed in Section 3.2.1. This leads to a detrimental effect on the fracture toughness for specimens containing 16.7 wt% of polyester and onwards. At these high polyester loadings, it is not possible to perform the SENB experiments due to the brittleness of the specimens. The specimens fractured during the production of a precrack.

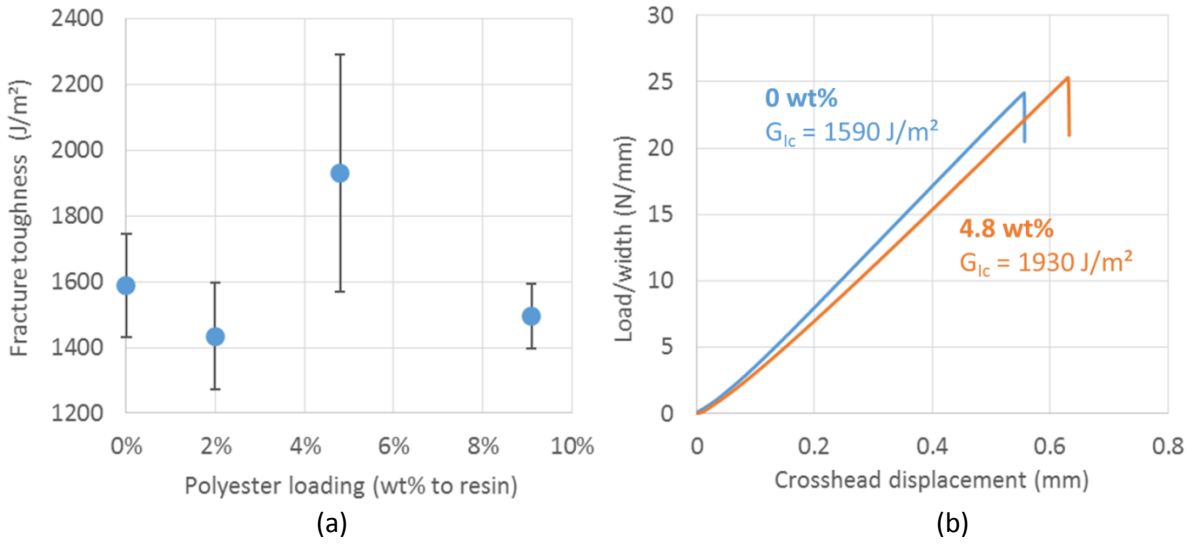

Figure 5: The fracture toughness of the bulk resin increases significantly when 4.8 wt% of polyester binder is added (a) as indicated by the larger area underneath the load-displacement curve (b).

The fracture surfaces of the SENB specimens show that high polyester loadings (16.7 wt% onwards) results in the formation of many polyester-rich globules due to phase separation, see Figure 6. No phase separation was visible in the virgin and 2 wt% specimens, while a sporadic polyester-rich globule was observed for specimens containing 4.8 wt% and 9.1 wt% of polyester. This phase separation at high polyester loadings is in accordance with the results obtained by DSC in Section 3.2.1: there is a limit to the amount of polyester which can be added to the epoxy resin without resulting in phase separation. This limit differs between the DSC and SENB experiments and is probably due to the difference in curing cycle. It is clear that a phase separation of the relatively brittle polyester binder results in a decrease in fracture toughness of the epoxy resin when the polyester-rich globules are present in large quantities and, thus, should be avoided in binder consolidated preformed laminates.

The increase in Mode I interlaminar fracture toughness of the GFRP laminates upon addition of the polyester binder to the glass fibres can be explained by the locally increased fracture toughness of the matrix resin. Especially the interlaminar regions are affected by the polyester binder which will result

locally in an increased failure strain of the resin due to the plasticizing effect of the polyester. Hence, the Mode I interlaminar fracture toughness increases. However, in the case where there is a large polyester-rich phase, the fracture toughness of the epoxy resin will be decreased substantially. This might explain the disastrous effect of a polyester binder on the interlaminar fracture toughness and mechanical properties reported in other research [6–10].

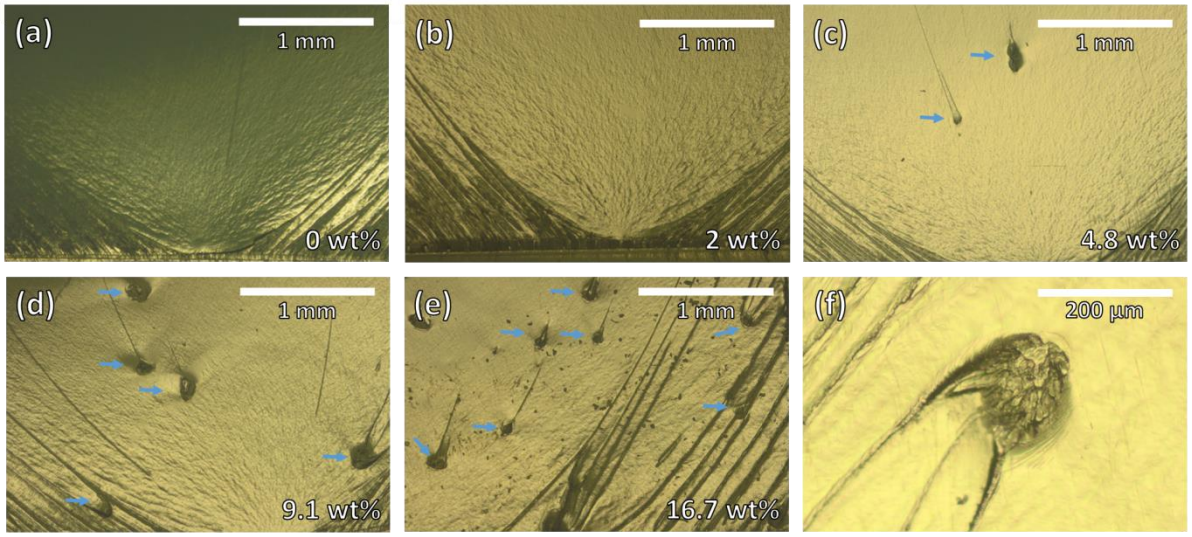

Figure 6: Optical microscopy images of the SENB fracture surface show polyester-rich globules (blue arrows) at high polyester loadings (a – e). A close-up of a polyester-rich globule (f).

4. CONCLUSION

Bisphenol A based polyester, commonly used for binder applications, is proven to be useful as an interlayer toughening system for VARTM produced composite laminates. DSC experiments show that the polyester is miscible in the epoxy resin at low amounts. At higher polyester loadings, a two phase morphology forms which consists out of polyester-rich globules in epoxy. SENB experiments indicate that these polyester-rich globules have a detrimental effect on the fracture toughness of the bulk epoxy matrix resin. In absence of polyester-rich globules, however, the polyester molecules act as a plasticizer which increases the flexibility of the epoxy resin network. This leads to a higher fracture toughness for epoxy resin containing 4.8 wt% of polyester (wt% to resin). Composite laminates are produced containing polyester coated glass fibre plies. The polyester is applied according to commonly used industrial binder loadings. Mode I interlaminar fracture increases by about 60 % for polyester modified composite laminates. The increase in interlaminar toughness is remarkable compared to the disastrous effect on interlaminar toughness reported in literature and is attributed to the increased flexibility of the plasticized epoxy network and a minimal presence of polyester-rich phase. Flexural properties are shown not to be affected by the presence of the polyester in the epoxy resin.

In conclusion, bisphenol A based polyesters can be used to produce binder consolidated preforms without negatively affecting the mechanical properties of the final laminates. Furthermore, the Mode I interlaminar fracture toughness can even be increased by as much as 60 % when an appropriate amount of polyester binder is used. Tailoring the epoxy resin type, the curing cycle and the polyester concentration to such a degree that the amount of polyester-rich phase is minimal can be necessary to obtain highly toughened composite laminates.

ACKNOWLEDGEMENTS

Financial support from the Special Research Fund (BOF) Ghent University is gratefully acknowledged. Results in this paper were obtained within the framework of the BOF 13/24J/020 project. We also thank COIM Group for providing commercial FILCO binders.

REFERENCES

[1] Wu W, Xie L, Jiang B, Ziegmann G. Influence of textile preforming binder on the thermal and rheological properties of the catalyzed cyclic butylene terephthalate oligomers. *Composites Part B: Engineering* 2013;55:453–62. doi:10.1016/j.compositesb.2013.07.005.

[2] Haider M, Hubert P, Lessard L. An experimental investigation of class A surface finish of composites made by the resin transfer molding process. *Composites Science and Technology* 2007;67:3176–86. doi:10.1016/j.compscitech.2007.04.010.

[3] Palardy G, Hubert P, Haider M, Lessard L. Optimization of RTM processing parameters for Class A surface finish. *Composites Part B: Engineering* 2008;39:1280–6. doi:10.1016/j.compositesb.2007.12.003.

[4] Tsotsis TK. Interlayer toughening of composite materials. *Polymer Composites* 2009;30:70–86. doi:10.1002/pc.20535.

[5] Hillermeier RW, Seferis JC. Interlayer toughening of resin transfer molding composites. *Composites Part A: Applied Science and Manufacturing* 2001;32:721–9. doi:10.1016/S1359-835X(00)00088-9.

[6] Tanoglu M, Robert S, Heider D, McKnight SH, Brachos V, Gillespie JW. Effects of thermoplastic preforming binder on the properties of S2-glass fabric reinforced epoxy composites. *International Journal of Adhesion and Adhesives* 2001;21:187–95. doi:10.1016/S0143-7496(00)00050-6.

[7] Tanoğlu M, Seyhan AT. Compressive mechanical behaviour of E-glass/polyester composite laminates tailored with a thermoplastic preforming binder. *Materials Science and Engineering: A* 2003;363:335–44. doi:10.1016/j.msea.2003.08.005.

[8] Tanoğlu M, Tuğrul Seyhan A. Investigating the effects of a polyester preforming binder on the mechanical and ballistic performance of E-glass fiber reinforced polyester composites. *International Journal of Adhesion and Adhesives* 2003;23:1–8. doi:10.1016/S0143-7496(02)00061-1.

[9] Brody JC, Gillespie JW. Reactive and non-reactive binders in glass/vinyl ester composites. *Polymer Composites* 2005;26:377–87. doi:10.1002/pc.20068.

[10] Brody JC, Gillespie JW. The Effects of a Thermoplastic Polyester Preform Binder on Vinyl Ester Resin. *Journal of Thermoplastic Composite Materials* 2005;18:157–79. doi:10.1177/0892705705043535.

[11] Allaer K, De Baere I, Van Paepegem W, Degrieck J. Direct fracture toughness determination of a ductile epoxy polymer from digital image correlation measurements on a single edge notched bending sample. *Polymer Testing* 2015. doi:10.1016/j.polymertesting.2015.01.014.